



Short communication

Improvement of activated carbons as oxygen reduction catalysts in neutral solutions by ammonia gas treatment and their performance in microbial fuel cells



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H I G H L I G H T S

- Ammonia treatment improved ORR catalytic activity at pH = 7.
- Oxygen content decreased 29–58% on the surface of treated ACs.
- Nitrogen content was increased up to 1.8% on the surface of treated ACs.
- Treatment increased the basicity of the bituminous, peat, and hardwood ACs.
- Cathode performance improved with all but one ammonia treated AC.

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Commercially available activated carbon (AC) powders from different precursor materials (peat, coconut shell, coal, and hardwood) were treated with ammonia gas at 700 °C to improve their performance as oxygen reduction catalysts in neutral pH solutions used in microbial fuel cells (MFCs). The ammonia treated ACs exhibited better catalytic performance in rotating ring–disk electrode tests than their untreated precursors, with the bituminous based AC most improved, with an onset potential of $E_{\text{onset}} = 0.12$ V (untreated, $E_{\text{onset}} = 0.08$ V) and $n = 3.9$ electrons transferred in oxygen reduction (untreated, $n = 3.6$), and the hardwood based AC (treated, $E_{\text{onset}} = 0.03$ V, $n = 3.3$; untreated, $E_{\text{onset}} = -0.04$ V, $n = 3.0$). Ammonia treatment decreased oxygen content by 29–58%, increased nitrogen content to 1.8 atomic %, and increased the basicity of the bituminous, peat, and hardwood ACs. The treated coal based AC cathodes had higher maximum power densities in MFCs (2450 ± 40 mW m⁻²) than the other AC cathodes or a Pt/C cathode (2100 ± 1 mW m⁻²). These results show that reduced oxygen abundance and increased nitrogen functionalities on the AC surface can increase catalytic performance for oxygen reduction in neutral media.

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1. Introduction

Microbial fuel cells (MFCs) are a promising option for reduction of energy costs associated with the treatment of wastewater sources [1]. Power production from MFCs is limited by the overpotential of the oxygen reduction reaction (ORR) at the cathode, which is negatively impacted by the conditions of neutral pH and ambient temperature common in MFCs. Depending on the catalyst properties, the ORR can proceed through either a 4e⁻ pathway producing water or hydroxide [2], or 2e⁻ pathway producing hydrogen peroxide as an intermediate [3]. Peroxides can be further reduced

through an additional 2e⁻ reduction step, resulting in a mixed reduction pathway that can approach an apparent four electron transfer to the cathode [3].

In order to achieve commercial viability, low cost materials are essential to the success of MFC technology. Activated carbons (ACs) are inexpensive ORR catalysts that can be made from several biomass waste materials such as coconut shells, wood chips and sawdust. They have a complex surface chemistry that can be tailored to improve their performance for the desired application. AC powder based cathodes have produced power densities in MFCs similar to or slightly higher than those made with a typical platinum catalyst. An MFC with an AC cathode, made using a polytetrafluoroethylene (PTFE) binder and a nickel current collector, produced 1220 mW m⁻², compared to 1060 mW m⁻² with cathodes made with a Pt catalyst and a Nafion binder [4]. MFCs with AC

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and a polydimethylsiloxane (PDMS) diffusion layer reached $1255\text{--}1310\text{ mW m}^{-2}$ compared to 1295 mW m^{-2} with a standard Pt and carbon cloth (Pt/C) cathode [5]. Another type of AC air cathode, made by rolling out an AC/PTFE layer on a stainless steel mesh current collector, produced between 1086 and 1355 mW m^{-2} with two different AC powders. Power production compared to a standard Pt/C cathode was not reported [6]. In another study, the power production in MFCs using cathodes made from AC powders with less strong acid ($\text{pK}_a < 8$) functional groups was generally higher ($1610 \pm 100\text{ mW m}^{-2}$ for a peat based AC) than those made from ACs with more strong acid groups ($630 \pm 10\text{ mW m}^{-2}$ for a hardwood based AC) [7].

Nitrogen incorporation on carbon surfaces has been shown to increase the catalytic activity and selectivity for oxygen reduction through a four electron pathway in both acidic and alkaline environments [3,8,9], but it has not been examined for activity in neutral pH solutions. Several studies have shown that the number of nitrogen functional groups on carbon surfaces can be increased by treatment with ammonia gas at elevated temperatures [3,10–12]. During the process of incorporating the nitrogen into the carbon structure, there is a corresponding reduction in acidic oxygen groups as the oxygen atoms are desorbed from the carbon surface as CO/CO_2 . This rearrangement of surface functional groups results in an increase in the basic properties of the carbon surface at the expense of acidic properties [12–17].

In order to improve the performance of AC cathodes in MFCs, ACs made from four different precursor materials were treated with a high temperature, ammonia gas in order to modify the surface chemistry by increasing the number of basic nitrogen groups and decreasing the number of acidic oxygen functional groups. The treated ACs were examined as catalysts for oxygen reduction in neutrally buffered solutions and compared to the untreated precursor ACs. Treated ACs were evaluated in terms of activity and selectivity using a rotating ring–disk electrode (RRDE) and linear sweep voltammetry (LSV). The catalytic activity observed, in conditions relevant to MFC operation ($\text{pH } 7$, 30°C), was then compared to the change in surface chemistry that included the relative abundance of surface oxygen and nitrogen functional groups. The results of the kinetic and chemical property analyses were compared to the power production produced using the ammonia treated ACs in the cathodes of MFCs, relative to power densities produced with Pt/C cathodes.

2. Experimental

2.1. Activated carbons and ammonia treatment

Four AC powders previously shown to function well as ORR catalysis [7] were chosen that spanned a range of typical physical and chemical characteristics in commercially available AC powders. The four ACs were: a peat based carbon, Norit SXPlus (P, Norit, USA); a coconut shell based carbon, YP50 (C, Kuraray Chemical, Japan); a hardwood carbon, Nuchar SA-1500 (W, MeadWestvaco, USA); and a bituminous coal carbon, CR325B (B, Carbon Resources, USA). The base ACs were treated with ammonia gas (5% in helium) at 700°C using a vertical cylindrical glass tube reactor in a programmable furnace (model 3210, Applied Test Systems, Inc., Butler, PA). Before heating, the furnace (including sample) was purged with ultrapure nitrogen gas for 30 min. Gas flow was changed to dilute ammonia while temperature was ramped at 5°C min^{-1} , then held at 700°C for 1 h. The furnace and sample were purged with ultrapure nitrogen gas while cooling to ambient temperature. The performance of these carbons (denoted as –N) in terms of ORR catalysis was compared to the base AC samples, as well as carbon

black XC-72 (CB), and Pt (10%) in carbon black XC-72 (PtC) (Fuel Cell Store, USA) in electrochemical tests.

2.2. Chemical surface analysis

The elements present on the surface of the AC powders were identified by X-ray photoelectron spectroscopy (XPS, Axis Ultra XPS, Kratos Analytical, UK, monochrome AlK α source, 1486.6 eV). A base survey scan was performed first, followed by a detailed scan of C1s (285–289 eV), O1s (531–536 eV), and N1s (398–406 eV) signals [18]. CASA XPS software was used for the elemental and peak fitting analysis.

Potentiometric titrations were performed using a DL53 automatic titrator (Mettler Toledo, USA) in the pH range of 3–11, with volumetric standard NaOH (0.1 M) used as the titrant and NaCl (0.01 M) as the electrolyte. Before titration, 0.2 g of AC was equilibrated with 100 mL of electrolyte adjusted to $\sim\text{pH } 3$ using HCl (0.1 M) and degassed with N_2 for 1 h. The experimental data were transformed into proton binding curves (Q , mmol g^{-1}) by subtracting out the blank titration values [19]. The proton binding curves were deconvoluted using the SAIEUS numerical procedure to obtain the distribution of acidity constants [20–22]. This analysis produces separate peaks that denoted different types of functional groups, with the area under the peak corresponding to the quantity of functional groups detected (mmol g^{-1}) based on binding/release of protons during titration.

2.3. Rotating ring–disk electrochemical analysis

Catalyst ink was prepared by adding 30 mg of the powdered sample to 3 mL of DMF and homogenized with a sonifier (S-450A, Branson, USA) fitted with a 1/8 inch micro tip, pulsed at 50% for 15 min, in an ice bath. Nafion (270 μL ; 5 wt% solution) was added and the solution was mixed for an additional 15 min. The ink solution (10 μL) was drop coated onto a 5 mm diameter glassy carbon disk (Pine Instruments, USA) and allowed to dry overnight. The disk was prepared before coating by polishing with 5.0 and 0.05 μm alumina paste and cleaned in an ultrasonic bath for 30 min.

All RRDE experiments were run first in nitrogen sparged solution in order to obtain the baseline current, before being switched to an air sparged 100 mM phosphate buffer solution (PBS) (9.13 g L^{-1} Na_2HPO_4 , 4.90 g L^{-1} $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.31 g L^{-1} NH_4Cl , and 0.13 g L^{-1} KCl; pH 7). Solutions were sparged for 30 min before LSVs were run, and then the gas was streamed into the headspace for the duration of the experiment. In order to clean the electrode surface of possible contaminants or excess oxygen trapped in the pores of the carbon, the disk potential was cycled between 0.4 and 1.0 V at 100 mV s^{-1} until a consistent current response was observed from one cycle to the next. All potentials are reported vs. 3 M Ag/AgCl reference electrodes (0.197 V vs. SHE). The potential of the disk electrode was then scanned from 0.4 to -1.0 V at 10 mV s^{-1} and rotation rates of 100–2100 rpm, while the potential of the platinum ring was held constant at 0.62 V for H_2O_2 oxidation. The potential sweeps at each rotation rate were repeated three times consecutively to ensure stability of the measurements. The current obtained under nitrogen sparging was subtracted from that obtained under air sparging to obtain the faradaic current attributed to oxygen reduction [23]. Catalyst activity was evaluated by the onset potential (E_{onset}) and limiting current (i_{lim}) [23]. The average number of electrons transferred (n) in the ORR at the disk electrode was calculated based on the amount of H_2O_2 detected using [24]

$$n = \frac{4i_{\text{disk}}}{i_{\text{disk}} + i_{\text{ring}}/N} \quad (1)$$

where i_{disk} is reduction current at the disk, i_{ring} the oxidation current at the ring, and N is the collection efficiency of the RRDE.

2.4. MFC experiments

AC cathodes (31 mg cm⁻² loading, projected surface area of 7 cm²) were constructed as previously described [5], except that two PDMS diffusion layers that were applied to the air side of the stainless steel mesh current collector (50 × 50 mesh, type 304, McMaster-Carr, OH) prior to application of the carbon catalyst layer [25]. In addition, a second stainless steel mesh current collector was pressed onto the solution side of the activated carbon to improve electrical conductivity of the cathode. AC powder was mixed with 10 wt% PTFE binder (in a 60% emulsion) and spread evenly onto the solution side of the PDMS coated mesh, and pressed at 4.54 metric ton-force for 20 min (Carver press, Model 4386, Carver Inc., IN) [5]. Pt-catalyzed air cathodes (projected surface area of 7 cm²) were constructed from carbon cloth (30 wt% wet proofing, Fuel Cell Earth LLC) with four PTFE diffusion layers, and a catalyst loading of 0.5 mg-Pt cm⁻² (on carbon black XC-72) [26] to benchmark AC cathodes against this commonly used cathode.

Cube-shaped MFCs were constructed as previously described [27]. The anode chamber was a 28 mL cylindrical chamber (7 cm² cross section) bored into a Lexan block. The anodes were carbon fiber brushes with a titanium wire core (2.5 cm diameter, 2.5 cm length, and 0.22 m² surface area) which was heat treated at 450 °C [28] and then placed horizontally in the center of the cylinder. The electrode spacing was 2.5 cm (from center of the anode to the cathode). The MFCs were inoculated using effluent from an MFC operated under conditions similar to those used here. The MFC medium was 100 mM PBS amended with vitamins and minerals [29] and 1 g L⁻¹ sodium acetate. Anodes were inoculated and acclimated under the same conditions in MFCs containing standard

Pt/C carbon cloth cathodes, and then tested with the different cathodes. A 1000 Ω resistor was used during acclimation, and then the resistance was changed to lower resistance (100 Ω) for several cycles before running polarization tests to avoid power overshoot [30]. All MFCs were operated at 30 °C in a constant temperature controlled room. Once the MFC produced a steady voltage for 3 cycles, the Pt/C cathodes were removed and replaced with the AC cathodes, CB cathodes, or new Pt/C cathodes. All MFC tests were conducted in duplicate.

The voltage across the resistor was recorded every 30 min using a multimeter (model 2700 Keithley Instruments, Cleveland, OH) with a computerized data acquisition system. Polarization curves were obtained by applying a different external resistance to the circuit for a complete batch cycle (multiple cycle method), and the

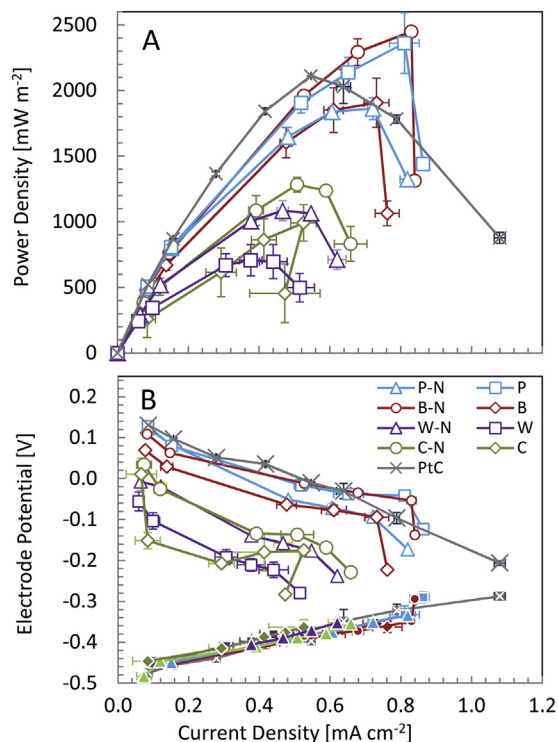


Fig. 1. A) Power densities and B) electrode potentials during cell polarization of MFCs using AC cathodes compared to Pt/C. (100 mM phosphate buffer; open symbols indicate cathode potentials, filled symbols anode potentials.)

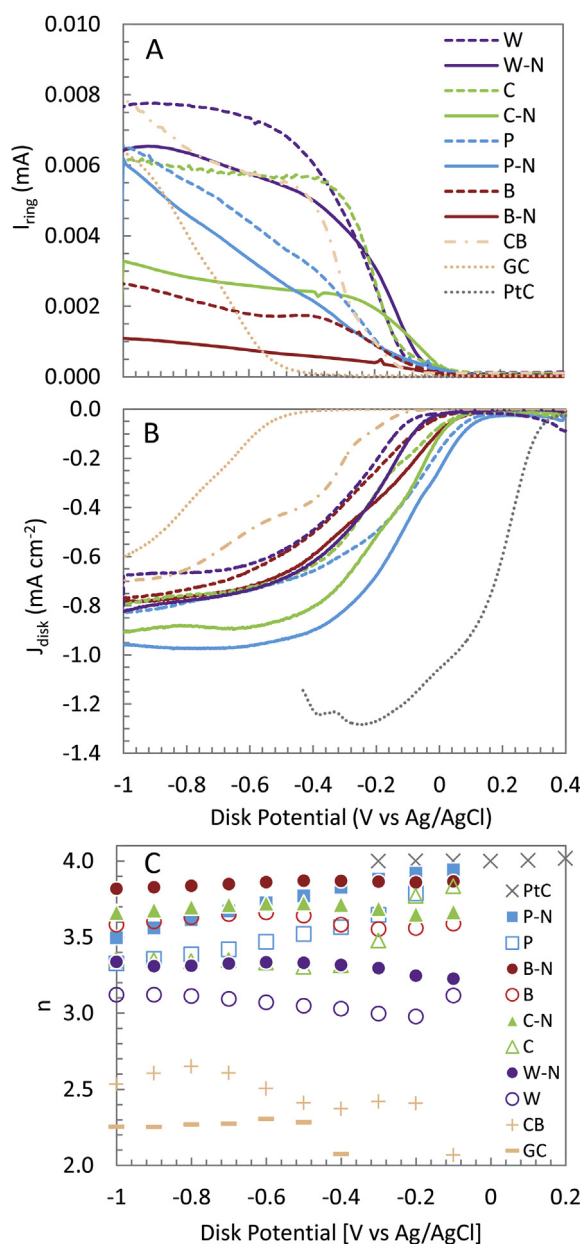


Fig. 2. A) H₂O₂ detection based on oxidation current at the Pt ring during oxygen reduction at the catalyst on the disk electrode. B) Oxygen reduction current response during LSV of AC catalysts at the disk electrode compared to Pt/C (100 mM phosphate buffer, 2100 rpm). C) Average number of electrons transferred (measured by RRDE analysis) during oxygen reduction.

average sustainable voltage was recorded for each resistance. Current density was calculated from $I = U/R$, where I is the current, U the measured voltage, and R the external resistance, and normalized to the projected cathode surface area. Power densities were calculated using $P = IU$, and normalized by the projected cathode surface area [31].

3. Results and discussion

3.1. MFC performance

In general, cathodes made from ammonia treated AC powders had higher maximum power densities in MFCs than cathodes made with the corresponding untreated AC (Fig. 1A). The highest power was obtained using the treated bituminous coal AC (B–N) cathode ($2450 \pm 43 \text{ mW m}^{-2}$; $0.83 \pm 0.01 \text{ mA cm}^{-2}$), which was a 28% increase in power compared to the MFC with the untreated bituminous AC (B) cathode ($1910 \pm 188 \text{ mW m}^{-2}$; $0.73 \pm 0.04 \text{ mA cm}^{-2}$), and a 16% improvement in maximum power compared to a standard Pt/C cathode ($2100 \pm 1 \text{ mW m}^{-2}$; $0.55 \pm 0.01 \text{ mA cm}^{-2}$). Treating the hardwood AC powder (W–N) produced the largest improvement, with 53% higher power production than the untreated hardwood (W). Ammonia treatment of the coconut AC (C–N) resulted in a 29% increase in maximum power. The peat-based cathodes were the exception to improved power with treatment, as the untreated peat AC (P) cathode had a higher power density of $2360 \pm 230 \text{ mW m}^{-2}$ ($0.81 \pm 0.04 \text{ mA cm}^{-2}$) than the treated AC (P–N) cathode ($1860 \pm 84 \text{ mW m}^{-2}$; $0.72 \pm 0.01 \text{ mA cm}^{-2}$).

Power and current densities of the untreated base ACs were higher than those in a previous study [7] due to the addition of a second stainless steel mesh current collector on the solution side of the cathode (Fig. S.1A). The higher maximum power densities resulted from increased working potentials of the cathodes (decreased cathode overpotential), since the anodes in all of the MFCs operated at similar potentials (Fig. 1B, Fig. S.1B). MFCs that produced the most power at a given current density had cathodes with the lowest overpotentials, such as the treated bituminous

sample (B–N) ($-0.05 \pm 0.00 \text{ V}$ at peak power), which had a 43% increase in working potential compared to the untreated AC.

3.2. Catalyst activity and selectivity

Ammonia treatment of the ACs improved catalytic activity for oxygen reduction in all samples based on evaluation using LSV and RRDE (Fig. 2). Despite the reduced power production observed in the MFC cathode tests, the ammonia treated peat-based AC (P–N) had the greatest oxygen reduction activity ($E_{\text{onset}} = 0.16 \text{ V}$ and $i_{\text{lim}} = 0.96 \text{ mA cm}^{-2}$ at 2100 rpm), and was improved from the untreated peat AC performance ($E_{\text{onset}} = 0.14 \text{ V}$ and $i_{\text{lim}} = 0.83 \text{ mA cm}^{-2}$). The other treated ACs had catalytic improvements that aligned with the increased power production observed in MFC tests. The treated bituminous coal (B–N) had a reduced overpotential and a similar limiting current ($E_{\text{onset}} = 0.12 \text{ V}$ and $i_{\text{lim}} = 0.78 \text{ mA cm}^{-2}$) compared to the untreated sample (B) ($E_{\text{onset}} = 0.08 \text{ V}$ and $i_{\text{lim}} = 0.76 \text{ mA cm}^{-2}$). The activity of the hardwood AC sample improved after ammonia treatment, with both a reduction in overpotential and an increase in oxygen reduction current activity (W–N, $E_{\text{onset}} = 0.03 \text{ V}$ and $i_{\text{lim}} = 0.82 \text{ mA cm}^{-2}$; W, $E_{\text{onset}} = -0.04 \text{ V}$ and $i_{\text{lim}} = 0.67 \text{ mA cm}^{-2}$). Even though the peat based (P) and ammonia treated bituminous (B–N) AC achieved higher power densities than standard Pt/C cathodes in MFC tests, all of the AC materials had less catalytic activity than the Pt/C catalyst in RRDE tests ($E_{\text{onset}} = 0.36 \text{ V}$ and $i_{\text{lim}} = 1.28 \text{ mA cm}^{-2}$), suggesting that mass transfer to the catalyst material is important for MFC performance.

The selectivity of the catalysts for a complete four electron reduction (and limited H_2O_2 production) was evaluated using RRDE, and the average number of electrons transferred (n) was calculated using an empirical collection efficiency of 0.2 (Fig. 2C). The selectivity of the catalyst improved after ammonia treatment for all of the samples tested. The treated bituminous (B–N) AC had the most consistent, near complete reduction of oxygen over the range of potentials with an average $n = 3.85$. The treated peat-based (P–N) AC catalyst was also near four electrons with $n = 3.9$

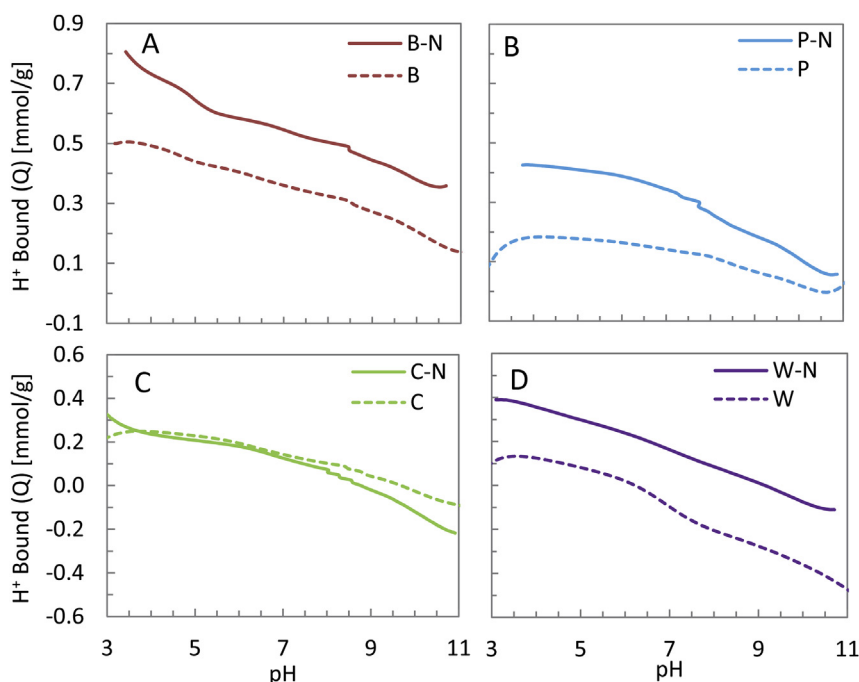


Fig. 3. Proton binding isotherms for treated (solid lines) and untreated (dashed lines) A) bituminous, B) peat, C) coconut shell, and D) hardwood based activated carbons.

at -0.2 V, but this tapered off to $n = 3.5$ as the disk potential was decreased to -1 V. Peroxide formation was detected by the platinum ring electrode for all of the ACs tested. This indicated that there was a mixed reaction pathway with some catalytic sites possibly reducing oxygen to $\text{H}_2\text{O}/\text{OH}^-$ through a direct four electron reduction, with others sites reducing oxygen to H_2O_2 through a two electron transfer route, and then a second reduction pathway where the peroxide product was further reduced to $\text{H}_2\text{O}/\text{OH}^-$ by an additional two electron reduction [3].

3.3. Effect of surface chemistry

Ammonia treatment of the AC samples increased the basicity of the carbon surface for the bituminous, peat, and hardwood based samples (Fig. 3) as expected based on previous studies [12–17]. PT analysis of the coconut based sample did not show a noticeable change in basic properties. Acidic oxygen functional groups could not be reliably quantified using this deconvolution of the proton binding isotherm because some nitrogen functional groups have $pK_{\text{as}} \sim 4.5$ and 9 [17]. However, the measured increase in the basicity is evidence that the heat treatment increased the relative amount of basic to acidic groups on the carbon surface.

Based on the XPS analysis, the ammonia treatment process successfully increased the amount of nitrogen groups present on the surface of the ACs to a measureable level (Fig. 4). The hardwood based AC incorporated the most nitrogen, and the type of nitrogen chemistry present was similar among all of the treated samples with more pyridine-like (398.5 eV), pyrrole-like (400 eV) and quaternary or graphitic nitrogen (401 eV) groups present, and to lesser extent nitrogen oxides (403–405 eV) [9,10,17,32,33]. From the quantitative analysis (Fig. 5), ammonia treatment reduced the relative abundance of oxygen atoms between 29 and 58% on the surface of all ACs, with the peat and hardwood losing the largest percent and the coconut shell AC losing the least. The corresponding gain in surface nitrogen groups resulted in nitrogen levels between 0.9 and 1.8 atomic %. The decrease in relative abundance of oxygen along with the increase in surface nitrogen groups resulted in the increase in catalytic activity for oxygen reduction observed through the increase in onset potential, current response, and increased electron transfer numbers nearing a net four electron reduction pathway. These results are similar to those reported for naphthalocyanine modified carbons in neutral buffer [24] and treated carbon nanofibers tested in an alkaline solution [3], where

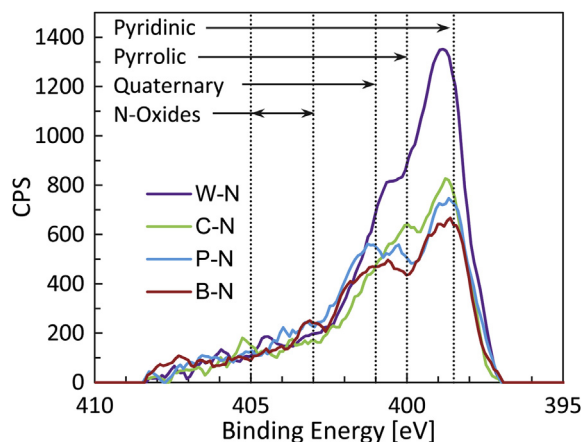


Fig. 4. N1s peaks on ammonia treated ACs from XPS show presence of nitrogen groups on the surface of the treated AC. Representative peak positions of nitrogen groups reported in literature are identified by dotted lines [9,10,17,32,33].

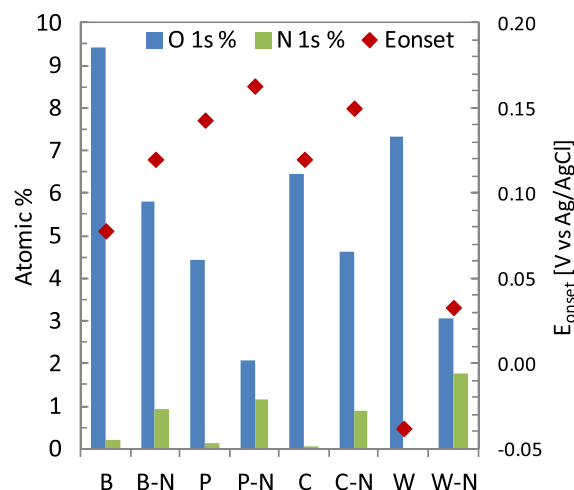


Fig. 5. Atomic % of oxygen and nitrogen on the surface of treated and untreated AC catalysts measured using XPS and the relationship to onset potential of the ORR measured with RRDE.

oxygen reduction at the electropositive carbon sites adjacent to nitrogen groups follow the Yeager Model which leads to a direct four electron reduction. This is in contrast to the Pauling model where end-on oxygen adsorption to the electropositive site at the carbonyl group leads to a two electron transfer and peroxide production, which can be further reduced through a sequential two electron pathway on any oxygen functional group [3].

4. Conclusions

Ammonia treatment of AC powders resulted in an increase in ORR catalytic activity and selectivity in a neutral phosphate buffer solution due to an increase in nitrogen and decrease in acidic oxygen surface functional groups. Selection of an ideal AC catalyst for neutral buffered environments, like those in MFCs, should therefore focus on the presence of surface nitrogen groups. Stability of the treated AC catalysts should be explored in MFC applications, possibly using XPS to detect changes in the surface chemistry, since increasing the basicity of AC surfaces has been shown to increase the adsorption of dissolved organic matter and other contaminants commonly found in wastewater. Adsorption of these molecules may block active surface sites, which can interfere with ORR catalysis [13,16]. Also, alternative methods for low cost, sustainable tailoring of ACs to achieve the desired surface chemistry should be explored.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.05.135>.

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